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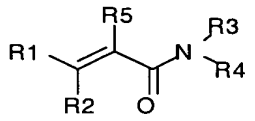
Method for production of α,β-unsaturated amide compounds

The present invention relates to methods for producing α,β-unsaturated amide compounds or methods for introducing an α,β-unsaturated double bond in compounds, which contain an amide grouping by dehydrating the corresponding saturated amide bond in the α,β-position.

The present invention relates to methods for production of α,β-unsaturated amide compounds having the general formula (I):



(I)

wherein

R_1 and R_2 are independently hydrogen; optionally linear or branched (C_1-C_{18}) alkyl or (C_1-C_{18}) alkenyl substituted with hydroxy, halogen, phenyl, substituted phenyl or an ester group [-C(O)OAlkyl] or an amide group [$-C(O)NH_2$ or -C(O)NHAlkyl]; optionally phenyl substituted with halogen; or

R_1 or R_2 is a group Y-R_6; wherein

Y is oxygen (-O-); sulphur (-S-); $-NR_7-$; or dialkylsilyloxy [$-(alkyl)_2Si-O-$];

R_6 is hydrogen, linear or branched (C_1-C_{18}) alkyl substituted optionally with hydroxy, halogen, phenyl,

substituted phenyl or with an ester group [-C(O)OAlkyl] or an amide group [-C(O)NH_2] or [-C(O)NHAlkyl]; optionally phenyl substituted with halogen;

R_7 is (C_1-C_{18}) alkyl or -N(R_6)(R_7) is a 5- or 6-membered heterocyclic ring;

or

R_1 together with R_3 is directly bonded or forms a group of the formula -$(CH_2)_n$-; wherein

n is a whole number from 1 to 12;

or

R_1 together with R_2 is cyclohexylidene;

or

R_1 together with R_5 and the incorporated (C=C)-double bond is cyclohexenyl;

or

R_1 together with R_5 and the incorporated (C=C)-double bond forms a group of a mono-unsaturated bi-cyclic ring;

R_3 is hydrogen, optionally linear or branched (C_1-C_{12}) alkyl substituted with phenyl, hydroxyl, or halogen, optionally carrying one or more oxygen atoms, (C_5-C_8)-cycloalkyl or (C_5-C_8)-cycloalkenyl, optionally carrying one or more oxygen atoms; optionally phenyl substituted with halogen or hydroxyl; or R_3 together with R_1 is directly bonded or forms a group of the formula -$(CH_2)_n$-;

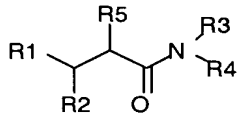
R_4 has one of the meanings of R_3, preferably hydrogen, optionally linear or branched (C_1-C_{12}) alkyl substituted with phenyl, hydroxyl, or halogen, optionally phenyl substituted with halogen or hydroxyl; or

-NR_3R_4 is a 5- or 6-membered heterocyclic ring; and

R_5 has one of the meanings specified for R_1 or R_2 as independent substituents [i.e. hydrogen; optionally linear or branched (C_1-C_{18}) alkyl or (C_1-C_{18})-Alkenyl substituted with hydroxy, halogen, phenyl, substituted phenyl, or an ester group [-C(O)OAlkyl] or an amide group [-C(O)NH_2 or -C(O)NHAlkyl]; or optionally, phenyl substituted with halogen];

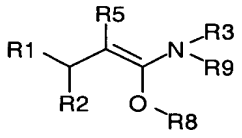
wherein said method comprises the steps of:

(A) reacting a compound of the general formula (II):



(II)

wherein R_1, R_2, R_3, R_4 and R_5 have the meanings given above, to introduce protective groups, so as to produce a compound with the general formula (III):



(III)

wherein

R_8 is trialkylsilyl, or (when R_4 = hydrogen) together with R_9 forms the group -C(O)-$(CH_2)_m$-C(O)- and

R_9 (when R_4 = hydrogen) is alkyloxycarbonyl or phenyloxycarbonyl, preferably Boc (= tert. butyloxy-carbonyl); or trialkylsilyl, or together with R_8 the group -C(O)-$(CH_2)_m$-C(O)-, and

m is 0, 1, 2, or 3, preferably 0 or 1, preferably 0,

and in the case in which for the compound of the general formula (II), hydroxyl is present, it is optionally reacted with a monovalent protective group R_8 and/or R_9;
(B) reacting the compound obtained in step (A) in presence of (i) a dehydrogenation catalyst and in presence of (ii) a suitable oxidising agent, such as optionally substituted benzoquinone, allylmethyl carbonate, allylethyl carbonate and/or allylpropyl carbonate,
to introduce an α,β-double bond in the α,β-position, and
(C) optionally, if present, removing the protective groups R_8, as well as the substituent R_9.

Suitable oxidising agents [in step (B)] include organic as well as inorganic compounds which form palladium compounds of the oxidation state +II from palladium compounds of the oxidation state zero. For example, allyl methyl carbonate reacts, as is known from the literature (Tetrahedron Letters, Vol. 25., No 42, 4783-4786, 1984) through oxidative addition at palladium(0) to form the corresponding palladium(II) allyl derivatives. Other oxidising agents with a similar effect are known to the person skilled in the art. It must be mentioned that in step (B) the substituent R_8 bonded to the amide unit through oxygen is removed at the same time.

R_1 and R_2 are independently, preferably hydrogen; optionally linear or branched (C_1-C_8) alkyl or (C_1-C_8) alkenyl, substituted with hydroxy, phenyl, with halogen or hydroxy substituted phenyl, or with an (C_{1-4})alkyl ester group [-C(O)O(C_{1-4})alkyl] or an amide group [-C(O)NH_2] or

(C_{1-4})alkyl amide group [$-C(O)NH(C_{1-4})$alkyl]; preferably, phenyl substituted with halogen; preferably linear or branched (C_1-C_8) alkyl or (C_1-C_8) alkenyl; benzyl or phenyl.

Preferably, R_2 is hydrogen and R_1 is preferably linear or branched (C_1-C_8) alkyl or (C_1-C_8) alkenyl; benzyl or phenyl or Y-R_6, where the definitions and constraints given further below are applicable for Y-R_6 or R_1 is hydrogen and R_2 has the broader meaning (specified for R_1).

Preferred are also the meanings, in which R_1 together with R_3 is directly bonded or is a group of the formula $-(CH_2)_n-$ and n is a whole number from 1 to 12; or R_1 together with R_2 stands for cyclohexylidene; or R_1 together with R_5 cyclohexenyl.

If either R_1 or R_2 stands for a group Y-R_6, then Y is preferably oxygen (-O-).

If R_1 together with R_3 is directly bonded or forms a group of the formula $-(CH_2)_n-$, then the compound of the formula (I) preferably stands for a lactam of an omega amino fatty acid, for example omega amino butyric acid (ω-butyrolactam), omega amino valeric acid (ω-valero-lactam), omega amino capronic acid (ω-caprolactam), or the omega amino lauric acid (ω-laurinolactam), which have an α,β-unsaturated double bond as per the compound of the general formula (I).

If R_1 together with R_5 and the incorporated (C=C)-double bond represents a monounsaturated bicyclic ring, then it is preferably a norbornyl group optionally substituted with hydroxyl or amino, preferably a norbornyl group.

R_3 preferably stands for hydrogen, optionally linear or branched (C_1-C_4) alkyl, cyclohexyl, substituted with phenyl; phenyl; or R_3 together with R_1 is directly bonded or forms a group of the formula $-(CH_2)_n-$.

R_4 preferably stands for hydrogen, optionally linear or branched (C_1-C_4) alkyl or phenyl substituted with phenyl, preferably hydrogen.

The group $-NR_3R_4$ is a heterocyclic ring preferably a pyrrolidine or piperidine.

R_5 preferably stands for hydrogen, tertiary butyl or phenyl substituted with halogen or hydroxyl, preferably hydrogen.

R_6 is preferably hydrogen, optionally linear or branched (C_1-C_8) alkyl substituted with hydroxy, halogen, phenyl, with halogen substituted phenyl, or with an (C_{1-4})alkyl ester group [$-C(O)O(C_{1-4})$alkyl] or an amide group [$-C(O)NH_2$] or (C_{1-4})alkyl amide group [$-C(O)NH(C_{1-4})$alkyl]; optionally phenyl substituted with halogen; preferably hydrogen, optionally linear or branched (C_1-C_8) alkyl substituted with phenyl or with an (C_{1-4})alkyl ester group or an amide group or an (C_{1-4})alkyl amide group; or phenyl;

preferably hydrogen, linear or branched (C_1-C_8)alkyl or phenyl.

R_7 preferably stands for (C_1-C_8) alkyl. The substituent $N(R_6)(R_7)$ stands for a heterocyclic ring preferably a pyrrolidine or piperidine group.

R_8 preferably stands for trimethylsilyl, or together with R_9 the group $-C(O)-(CH_2)_m-C(O)-$, in which m stands for 0, 1, 2, or 3, preferably 0 or 1, preferably zero.

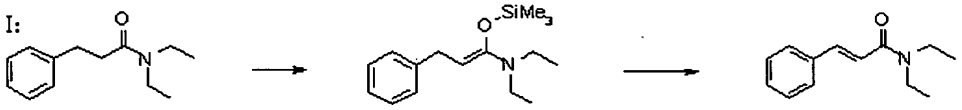
R_9 is alkyloxycarbonyl preferably isobutyloxy-carbonyl, tert. butyloxycarbonyl, tert. amyloxycarbonyl, cyclobutyloxycarbonyl, 1-methylcylobutyloxycarbonyl, cyclopentyloxycarbonyl, cyclohexyloxycarbonyl, 1-methyl-cyclohexyl, preferably tert. butyloxycarbonyl.

Dialkylsilyl preferably stands for dimethylsilyl. Trialkylsilyl preferably stands for trimethylsilyl. Halogen preferably stands for fluorine or chlorine, preferably fluorine. An alkyl ester group preferably stands for a methyl-, ethyl-, propyl- or butylester group. An alkyl amide group preferably stands for a methyl-, ethyl-, propyl- or butyl amide group.

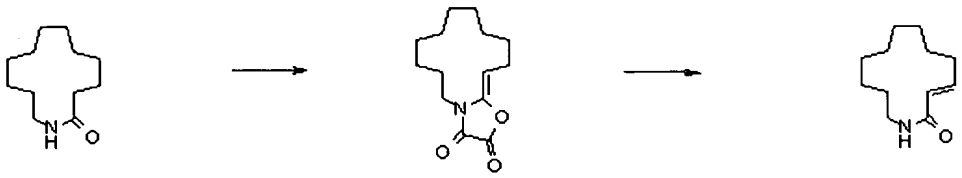
Compounds, which are produced as per the invention and which can be included under the general formula (I) are, for instance, the corresponding α,β-unsaturated compounds of N,N-dialkyl alkylamides, such as N,N-dimethylbutylamide

and homologous compounds, or of the lactams mentioned earlier. Other examples for production of α,β-unsaturated amide compounds as per the invention are:

I:



II:



For introducing the protective group trialkylsilyl, i.e. for silylation of the NH-group and/or of the oxygen atom or the OH group [as per step (A)], one preferably uses an $(alkyl)_3Si(halogen)$, such as $(CH_3)_3SiCl$, or bis-trimethylsilyltrihalogen acetamide, bistrimethylsilyl acetamide, hexamethyldisilazane and/or bistrimethyl urea, preferably bistrimethylsilyl-trifluoroacetamide, or a trialkylsilyl-trifluoromethane sulphonate, preferably trimethylsilyl-trifluoromethane sulphonate. The reaction conditions for the silylation are known from EP 0 473 226.

For introducing a protective group, in which R_7 together with R_8 stands for the group $-C(O)-(CH_2)_m-C(O)-$ and in which m has the notations specified earlier, one converts the compound of the general formula (II) or the lactam grouping [as per step (A)] with the corresponding dihalogenide, preferably oxalylchloride (oxalic acid

chloride) or malonyl chloride (malonic acid chloride), where oxalyl chloride is preferred. The reaction conditions for the conversion with oxalyl chloride are known from EP 0 428 366 and are to be used for the conversion with malonyl chloride or in the same way for similar reacting compounds.

For introducing a protective group, in which R_8 stands for alkyloxy carbonyl, such as tert. butyloxycarbonyl (Boc), one proceeds in a known way by converting the compounds of the general formula (II) with for example Boc anhydride (Boc O-Boc) $\{[(CH_3)_3C\text{-}O\text{-}C(O)]_2\text{-}O\}$ or with Boc carbamate $[(CH_3)_3C\text{-}O\text{-}C(O)\text{-}N(C_{1\text{-}4}\ \text{alkyl}\ )_2]$. Thereby, Boc is the representative for compounds reacting in a similar way, that is the compounds, in which the tert. butyl group is replaced by another similar reacting group, such as the mentioned groups of tert. amyl, cyclobutyl, cyclopentyl or cyclohexyl. Such analogous reactions find numerous mentions in the technical literature. If R_8 stands for trialklylsilyl and R_9 for Boc, then one introduces first the protective group Boc and thereafter silylates.

In step (B) the compound obtained in step (A) is reacted in the presence of (i) a dehydrogenation catalyst and (ii) in the presence of a suitable oxidising agent, like optionally substituted benzoquinone, allyl methyl carbonate, allyl ethyl carbonate and/or allyl propyl carbonate, to introduce the α,β-double bond in the α,β position.

The dehydrogenation catalyst is selected preferably from compounds (salts and complexes) of the group of the transition metals of the periodic system, in particular from the compounds of the metals of the group VIII. of the periodic system, in particular from iron (Fe), ruthenium (Ru) and osmium (Os); cobalt (Co), rhodium (Rh), and iridium (Ir); nickel (Ni), palladium (Pd) and platinum (Pt) as well as the group IB, i.e. of copper (Cu), silver (Ag) and gold (Au). Preferred are the compounds of the metals of the group VIII of the periodic system. Preferred are especially compounds or dehydrogenation catalysts based on rhodium (Rh), palladium (Pd) and platinum (Pt). Preferred are palladium compounds. Examples of such palladium compounds are: Pd(0)-compounds such as tris(dibenzylidene acetone)-dipalladium chloroform complex and Pd(II) compounds such as $PdCl_2$, $Pd(dppe)_2$, [dppe = bis-(1,2-biphenylphosphino)ethane], $Pd(dppe)Cl_2$, $Pd(OAc)_2$, $Pd(dppe)(OAc)_2$, π-allyl Pd-complexes, preferably π-allyl Pd chloride dimer. Preferred are Pd(0) compounds, especially tris(dibenzylidene acetone)dipalladium chloroform complex. These compounds, or salts and complexes, are well known and are described in the literature.

For thermal stabilisation of the palladium complex an additional complexing agent such as 2,2'-bipyridyl or 1,10-phenanthroline can be used, preferably 2,2'-bipyridyl.

As quinone, one can also use a substituted quinone, such as a quinone substituted with C_{1-4} alkyl, halogen, cyano or nitro. Such quinones are well known.

For explanation, it can be added for the mechanism of the catalysis, that a Pd-species adds at the C-atom in 2-position under splitting of the oxygen protective group [e.g. the $-Si(CH_3)_3$-group]. A subsequent beta-hydrogen splitting at the C-atom in 1-position leads to the desired Δ^1-double bond in 1-/2-position, and releases another palladium species, which is fed back in the catalytic cycle. Instructions for this reaction mechanism are given in the Tetrahydron Letters, page 4783, (1984). However, the present invention does not relate to this explanation.

In step (C) the compound obtained is then converted to the compound having the formula (I) by removal of the protective groups. This takes place preferably through a treatment with a suitable acid, such as with formic acid, acetic acid and/or trifluoroacetic acid, preferably with formic acid. Methods for isolating the compounds of the general formula (I) from the reaction mixture as well as for their further purification are known to persons skilled in the art. Thereafter, the compounds obtained can be further processed.

For the described methods with the steps (A)-(C), numerous dry organic solvents, such as toluene, benzine, hexane, heptane, tert. butyl alcohol, diethylether, acetone, benzene, dioxane, tetrahydrofuran, chloroform,

dimethylformamide or pyridine, may be used which are free of water.

The following examples illustrate the invention.

Example 1 (Production of an α,β-unsaturated butyramide, i.e. but-2-enoic acid dimethylamide)

Step 1A (Production of butyramide silylenolether, i.e. dimethyl-(1-trimethylsilanyloxy-but-1-enyl)-amine).

46 ml of a 2 molar (2M) lithium di-isopropylamide solution (LDA solution) is added carefully to a solution of 10 g (0.085 Mol) N,N-dimethylbutyramide and 54 g absolute tetrahydrofuran (THF) at an internal temperature of -80°C and stirred for about 1 hour at -70 to -80°C. Thereafter, at the same internal temperature 28 g (0.255 Mol) trimethylchlorosilane is added. Thereby, LiCl precipitates out. After adding the silane the cold bath is removed. One lets the mixture warm up to the ambient temperature overnight under nitrogen (N_2). At an internal temperature of 70-90°C the reaction mixture is distilled under N_2 flow, thereby about 8 g of the desired silyl enol ether accumulates in the sample.

^{1}H-NMR (200MHz, $CDCl_3$, δ): 3.48-3.38 (1H, t); 2.28(6H, s); 1.89-1.72(2H, m); 0.77 (3H, t); 0.02 (9H, s)

Step 1B (Production of α,β-unsaturated butyramide, i.e. but-2-enoic acid dimethylamide).

2 g (8 mMol) of the silyl enol ether from step 1 is heated under nitrogen with 16 g absolute acetonitrile, 2 g chloroform, 2.9 g (0.024 Mol) allyl methyl carbonate and 0.16 g (0.16 mMol) of the Pd catalyst to the reflux temperature (internal temperature 75-80°C). Already during heating, a clearly visible gas formation sets in. The dark green solution is stirred overnight. The black suspension

thus obtained is filtered and is concentrated under reduced pressure (only up to p=80 mbar). One gets about 0.9 g of unsaturated butyramide.

^{1}H-NMR (200MHz, $CDCl_3$, δ): 6.88-6.72 (1H, m); 6.20(1H, d broad); 3.04 (3H, s); 2.98 (3H, s); 1.78(3H, d);
MS (+EI): 114 (M+1, 40%); 98 (100%)

In the same way, as described above, 4-dimethylcarbamoyl-2,2-dimethyl-butyric acid methyl ester can be converted into 4-dimethylcarbamoyl-2,2-dimethyl-but-3-enoic acid methyl ester.

Example 2 (Production of α,β-unsaturated valerolactam, i.e. 6-oxo-3,6-dihydro-2H-pyridine-1-carboxylic acid tert-butyl ester)

Step 2A (Production of N-bocylated valerolactam, i.e. 2-oxo-piperidine-1-carboxylic acid tert-butyl ester)
55 ml of a 2M LDA solution is added carefully to a solution of 10 g (0.097 Mol) δ-valerolactam and 44.5 g absolute THF at an internal temperature of -60°C and stirred for about 1 hour at -60 to -70°C. Thereafter, at the same internal temperature, one adds drop wise a solution comprising 22.22 g (0.102 mol) boc anhydride and 18 g absolute THF and lets the reaction mixture warm up to the ambient temperature overnight. The mixture thus obtained is added to a mixture comprising 50 g toluene and 100 g water and stirred for about 30 minutes. The red, organic phase is washed three times each with 50 g water and then concentrated through distillation, as far as

possible, under reduced pressure. This results in 19 g of a dark oil.

^{1}H-NMR (200MHz, $CDCl_3$, δ): 3.78-3.55 (2H, t); 2.55-2.42(2H, t); 1.90-1.72 (4H, m); 1.57-1.48 (9H, s)

MS: 199 (M, <1%); 144 (46%); 57 (100%)

Step 2B (Production of boc-valerolactam-silyl enol ether, i.e. 6-trimethylsilanyloxy-3,4-dihydro-2H-pyridine-1-carboxylic acid tert-butyl ester)

30 ml of a 2M LDA solution is added carefully to a solution comprising 12 g (0.052 mol) of N-boc-valerolactam from step 1 and 44.5 g of absolute THF at an internal temperature of -60°C and stirred for about 1 hour at -60°C to -70°C. Thereafter, at the same internal temperature, 6.2 g (0.057 mol) of trimethylchlorosilane is added. LiCl thereby precipitates out. After adding the silane, the cold bath is removed. One lets the mixture warm up to the ambient temperature under N_2. The reaction mixture is then poured into a mixture comprising 50 g toluene and 50 g water, stirred briefly and the organic phase is washed three times, each time with 50 g water. After concentration, 14 g of a clear oil remains in the flask.

^{1}H-NMR (200MHz, $CDCl_3$, δ): 4.12 (1H, t); 3.03 (2H, t); 1.92-1.81 (2H, m); 1.55-1.40 (2H, m); 1.27(9H, s); 0.01 (9H, s)

Step 2C (α,β-unsaturated valerolactam, i.e. 6-oxo-3,6-dihydro-2H-pyridine-1-carboxylic acid tert-butyl ester)

2g (0.0074 Mol) of the silyl enol ether from state 2 is stirred together with 25 g of absolute acetonitrile, 0.4 g Pd catalyst and 0.8 g p-benzoquinone overnight at room temperature. The black reaction mixture obtained is vigorously stirred with 50 g of 5% NaOH solution, extracted with 50g of toluene and the organic phase is concentrated as far as possible. About 1 g of freely moving, dark oil remains in the flask.

^{1}H-NMR (200MHz, $CDCl_3$, δ): 6.82-6.72 (1H, m); 5.97(1H, d); 3.88 (2H, t); 2.46-2.35 (2H, m); 1.54 (9H, s)

Example 3 (N,N-diethyl-3-phenyl-acrylamide)

Step 3A (N,N-diethyl-(3-phenyl-1-trimethylsilanyloxy-propenyl)amine)

In 15 ml of tetrahydrofuran 3.3 ml of di-isopropylamine is added under cooling (-78°C) with 9.25 ml of 2.5 M hexyl-lithium solution. After 30 min 4.11 g (20 mmol) of N,N-diethyl-3-phenyl-propionamide is added. After further 60 minutes 7.6 ml of trimethylchlorosilane is added. The reaction mixture is left overnight to warm up to room temperature. Under reduced pressure (approx. 0.6 mbar), 3.55 g (64% of the theor.) N,N- diethyl-(3-phenyl-1-trimethylsilanyloxy-propenyl)amine (intermediate product) is obtained through distillation at 125-128°C, which can be used in step 2 without further purification.

Step 3B (N,N-diethyl-3-phenyl-acrylamide)

A solution of 20 ml acetonitrile, 1.35 ml chloroform, 2.63 ml allyl methyl carbonate, 0.15 g tris-(dibenzylide-acetone)dipalladium chloroform complex and 2.1 g of the intermediate product made above is boiled overnight at reflux. The reaction mixture is filtered clear and concentrated in vacuum. The remaining group contains 1.2 g N,N-diethyl-3-phenyl-acrylamide.

MS (eI): 204 (5%), 203 (M^+, 35%), 188 (18%), 131 (100%)

Example 4 (azacyclotridec-3-en-2-on)

Step 4A (4,5,6,7,8,9,10,11,12,13-decahydro-1-oxa-3a-aza-cyclopentacyclotridecene-2,3-dione)

At room temperature, 19 g (0.13 mol) of oxalyl chloride is added to a solution of 19.7 g (0.1 mol) of laurino-lactam in 400 ml toluene. The reaction mixture is stirred for 3 hours at 55°C and subsequently concentrated in vacuum. The group is crystallised with 300 ml heptane. About 21.4 g (85% of the theor.) of the intermediate product (4,5,6,7,8,9,10,11,12,13-decahydro-1-oxa-3a-aza-cyclopentacyclotridecene-2,3-dione) is obtained.

^{1}H-NMR (200MHz, $CDCl_3$, δ): 5.11 (2H, t); 3.73-3.67 (2H, m); 2.25-2.20 (2H, m); 1.70-1.29 (16H, m).

^{13}C-NMR (50MHz, $CDCl_3$, δ): 156.4; 151.6; 142.0; 40.4; 28.4; 27.4; 26.8; 26.7; 25.9; 25.4; 24.4; 24.1; 23.9.

Step 4B (azacyclotridec-3-en-2-on)

A mixture of 1.0 g(4 mmol) of the just produced intermediate product (4,5,6,7,8,9,10,11,12,13-decahydro-1-oxa-3a-aza-cyclopentacyclotridecene-2,3-dione), 1.4 g of allyl methyl carbonate, 5.9 g chloroform, 0.1 g tris-(dibenzylide acetone)dipalladium chloroform complex and 10 ml acetonitrile are boiled at reflux. After 4 hours and 16 hours additional 0.1 g tris-(dibenzylidenacetone)-dipalladium chloroform complex is added. The reaction mixture is concentrated after 2 days of boiling, dissolved in 20 ml of methanol and stirred at 0°C with 8 mmol sodium methylate (dissolved in 1.5 ml methanol) during 1 hour, and then concentrated in vacuum. The residue is diluted with acetic acid ethyl ester and washed with 1 N hydrochloric acid. The organic phase is concentrated. About 1.2 g of group remains comprising 6% laurinolactam, 5% azacyclotridec-3-en-2-on, 11% 3-allyl azacyclotridecan-2-on, 47% intermediate product (4,5,6,7,8,9,10,11,12,13-decahydro-1-oxa-3a-aza-cyclo-pentacyclotridecene-2,3-dione), 25% 14-allyl 4,5,6,7,8,9, 10,11,12,13-decahydro-1-oxa-3a-aza-cyclopentacyclo-tri-decene-2,3-dione and 6% dibenzylidene acetone. The products are separated chromatographically (silica gel, acetic acid ethyl ester/hexane).

Azacyclotridec-3-en-2-on: MS (eI): 195 (M^+, 18%), 167 (18%), 152 (18%), 150 (20%), 124 (46%), 81 (100%).

3-allyl azacyclotridecan-2-on: MS (eI): 237 (M^+, 50%), 207 (38%), 196 (65%), 55 (100%).

14-allyl 4,5,6,7,8,9,10,11,12,13-decahydro-1-oxa-3a-aza-cyclopentacyclotridecene-2,3-dione: ^{1}H-NMR (200MHz, $CDCl_3$,

δ): 5.5.3 (1H, ddt), 5.09 (1H, d); 5.08 (1H, d); 3.85 (1H, ddd); 3.76 (1H, ddd); 2.57 (1H, dd); 2.49 (1H, dd); 2.56-1.00 (18H, m).

MS (eI): 250 (M^+-allyl, 80%), 207 (100%).

In a similar way, the α,β-unsaturated compound 4a,5,6,7,-8,8a-hexahydro-1H-quinolin-2-on can be obtained from octahydro-quinoline-2-on.